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METHOD FOR PRODUCING POLYURETHANE FOAMS  
[VERFAHREN ZUR HERSTELLUNG VON POLYURETHANSCHAUMSTOFFEN]

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Method for Producing Polyurethane FoamsDescription

The invention concerns a method for producing polyurethane foamed materials by converting isocyanates with compounds that are reactive with respect to isocyanates in the presence of blow agents and if required catalysts, additives and/or auxiliary agents as well as the use of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes into polyurethane foamed materials.

The production of polyisocyanate polyaddition products, for example, polyurethanes, which may contain urea and/or isocyanurate structures, by converting polyisocyanates with compounds that are reactive with respect to isocyanates in the presence of catalysts that accelerate the reaction of the substances that are reactive with respect to isocyanates and if required blow agents, additives and/or auxiliary agents is generally known.

Just like other plastics, isocyanate polyaddition products are subjected to aging processes, which lead in general as time passes to a deterioration of the performance characteristics. Fundamental aging influences

are, for example, hydrolysis, photooxidation and thermooxidation, which lead to bond cleavages in the polymer chain. Especially the effect of humidity and even more the combination of humidity and high temperature have as a consequence a hydrolytic cleavage of the urethane and urea bonds in polyisocyanate polyaddition products, for example, polyurethanes, which will also be called PUR in the following.

This cleavage becomes apparent, not only in the significant deterioration of the performance characteristics, but also leads to the formation of aromatic amines, such as, for example, toluylene diamine (TDA) and diaminodiphenyl methane (MDA) or aliphatic amines, such as, for example, hexamethylene diamine or isophorone diamine.

As was determined in the tests, the amine formation is influenced by a series of parameters. Especially high temperatures starting at 80°C in combination with high air humidity lead to the hydrolytic cleavage of the urethane and urea bonds. These conditions are of importance for a few special application sectors of PUR soft foam materials.

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Another parameter that influences the formation of primary amines is the type and amount of the used catalysts.

As it was possible to demonstrate in diverse experiments, the catalysts contained in polyurethane systems, which are necessary for the urethanization and blow reaction, catalyze to a great extent also the hydrolytic inverse cleavage reaction. The presence of catalysts is thus a very decisive prerequisite for the hydrolysis of urethane and urea bonds. In addition, it was possible to show that the efficiency of the hydrolysis depends to a great extent from the activity and type of catalyst, as well as from if the catalyst remains in the system or can migrate out of the material. Tertiary amine catalysts with reactive functional groups, such as OH and  $\text{NH}_2$ , accelerate in particular the amine formation by considerably lowering the activation energy for the cleavage reaction. The functional groups bring about the integration of the catalysts in the produced PUR network and the products produced therewith have the advantage of having lower odor and fogging problems, since the catalysts cannot escape by diffusion after the PUR product is finished. The same applies to formulations with polyols, which were produced with primary and secondary amines as starter molecules and are thus available in catalytically active form in the foam. These polyols have recently found increased utilization. The formation of primary amines as cleavage products cannot

be excluded in formulations having components that are exposed to particularly humid and hot conditions due to their special application. In foamed materials with amine catalysts that do not contain any functional groups that can be incorporated, these escape instead as a rule already a short time after they are finished or when the foamed material ages. Humid and hot conditions lead to particularly low amine contents in these foamed materials.

In order to prevent the formation of primary amines, especially in PUR products that are exposed to humid and hot conditions, it became necessary to find additives that convert into chemically harmless compounds as cleavage products with primary amines. The additives should not noticeably influence the foaming reaction.

As compounds, which reduce the content of primary aromatic amines in polyurethane soft foamed materials, are utilized sterically inhibited cycloaliphatic monoisocyanates and monothioisocyanates according to United States patent 4,211,847, GB 1,565,124 and DE-A 2946625. The isocyanates react only to a limited extent due to their steric inhibition and their reactivity during the foamed reaction, which is lower in comparison to aromatic

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isocyanates, so that free isocyanate is available for a reaction with eventually existing aromatic amines after the foaming reaction has ended. What is disadvantageous of these teachings is that the mentioned compounds are relatively expensive and especially the two last mentioned compounds participate at least in part in the urethanization reaction despite their steric inhibition, and do not react only after the foaming reaction with the formed amine. In addition, these isocyanates tend to migrate out of the finished foam due to their low vapor pressure and represent thus a further health hazard due to the occurrence of free isocyanate.

In United States patent 5,821,292 are described 3-aryl acrylic acid esters as light stabilizing agents, antioxidants, and heat protection agents for organic polymers. There is no mention in this publication of an improvement of the hydrolytic stability and in particular a reaction with primary aromatic and aliphatic amines.

DE-A 42 32 420 discloses the utilization of  $\alpha,\beta$ -unsaturated ester carboxylates for the production of polyurethane foamed materials having an improved compression hardness and elongation at break. Salts of  $\alpha,\beta$ -unsaturated ester carboxylates are utilized herein as catalysts for the NCO/water reaction. In a subordinate



clause is explained that the compounds are able to add amino groups, which are produced during the slow foam aging process, due to the presence of olefinic double bonds in the neighborhood of the carboxylate groups. What is disadvantageous of these compounds is their catalytic effect, which leads to a disturbance of the foaming reaction. The catalytic effect of additives for the reduction of amine contents in finished PUR foams is however not desired, since this leads to a further and accelerated formation of primary amines, as explained above.

It is an object of the invention to develop methods for the production of polyurethane foamed materials, which can have if required isocyanurate and/or urea structures, preferably polyurethane soft foamed materials, by converting isocyanates with compounds that are reactive with respect to isocyanates in the presence of blow agents and if required catalysts, additives and/or auxiliary agents, which make possible the conversion of primary amines produced in particular by hydrolytic cleavage of urethane and urea bonds by means of a chemical reaction. Additives should in particular be found, which are able to reduce the content of primary, preferably primary aromatic amines, in PUR soft foamed materials. The amine scavengers

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should be as cost effective as possible and be easy to obtain and should be able to unfold their effect without further treatment in the finished foam. The compounds (i) should preferably not have an excessively low vapor pressure in order to prevent migration out of the foamed material.

It was only possible to attain this object by carrying out the conversion in the presence of at least one of the following compounds (i):  $\alpha,\beta$ -unsaturated carboxylic acid,  $\alpha,\beta$ -unsaturated carboxylic acid derivative,  $\alpha,\beta$ -unsaturated ketone and/or  $\alpha,\beta$ -unsaturated aldehyde.

A bonding of the free amines that may have been produced through an undesirable cleavage of urethane and/or urea bonds is achieved as a result of the use of (i) according to the invention by means of a reaction with compounds (i) according to the invention.

Primary as well as secondary amines are enabled for addition to C=C double bonds, in particular when the latter are in the vicinity of a carbonyl group. The addition of the amine called after Michael is carried out therein on the unsaturated system, in which the  $\pi$ -electrons are delocalized via the carbonyl group. As was determined in experiments, the temperatures from 70 to 120°C, which can occur under humid and hot conditions, for example, in a hot

steam sterilization or cleaning with hot steam, are surprisingly sufficient in order to at least partially convert the primary amine formed by means of hydrolytic cleavage of urethane and urea bonds in the PUR foamed material with the compounds (i) according to the invention.

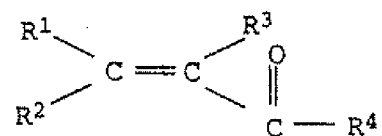
The compounds (i) are thus used in polyurethane foamed materials for reaction with amino groups. The amino groups are bonded to the  $\alpha,\beta$ -unsaturated carbonyl compounds by addition to the C=C double bonds and form a covalent bond on the  $\alpha,\beta$ -unsaturated carbonyl compounds according to the invention. The diffusion or migration of primary amines from the polyurethane foamed materials can be reduced therewith according to the invention. This applies in particular when the compounds (i) are incorporated into the produced polyurethane network through the presence of groups that can be incorporated, such as, OH or NH<sub>2</sub>. In this way, the compounds (i) are not only fixed, but their diffusion from the polyurethane foamed materials is fixed, and their diffusion out of the polyurethane foamed materials is not only prevented in this way, but also that of the primary amine bonded to the compound (i).

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As (i) can be utilized in general known  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic

acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes.

Compounds (i), which have the following general structural feature, are preferred:



with the following meanings for the radicals R1 to R4:

R<sup>1</sup>: H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,

R<sup>2</sup>: H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,

R<sup>3</sup>: H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,

R<sup>4</sup>: H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-OH, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-OH, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl,  
 -(C<sub>1</sub>-C<sub>12</sub>)-alkyl-NH<sub>2</sub>, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-NH<sub>2</sub>, -O-benzyl, O-aryl,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-COOH, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-CH(OH)-CH<sub>2</sub>-O-(CO)-  
 CHCH<sub>2</sub>, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-O-(CO)-CHCH<sub>2</sub>, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-  
 CH(OH)-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-CH(OH)-CH<sub>2</sub>-O-(CO)-  
 CHCH<sub>2</sub>.

The following compounds are particularly preferred as (i): acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-(acryloyloxy)-2-hydroxypropyl-methacrylate, cinnamic acid benzyl ester, trans-3-nonene-2-one, benzalacetone, dibenzalacetophenone, 1-methyl benzalacetone,

crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or  $\alpha,\beta$ -unsaturated polyester diols produced by means of polycondensation from maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols, such as butandiol, diethylene glycol, propylene glycol, 1,3-propandiol and/or triols, such as glycerin, with a molecular weight factor per double bond of 150 to 3000, a functionality of 2 to 6, a hydroxyl number of 20 to 800, and an acid number of 0 to 15.

The following compounds are used in particular as (i): Hydroxy ethyl acrylate, 3-(acryloyl-oxy)-2-hydroxy propyl methacrylate, trans-3-nonene-2-one, cinnamic acid benzyl ester, crotonic acid and/or  $\alpha,\beta$ -unsaturated polyester diols (A) produced by means of polycondensation of maleic acid, fumaric acid, methacrylic acid or acrylic acid with oligomeric diols, such as butandiol, diethylene glycol, propylene glycol, 1,3-propandiol and/or triols, such as glycerin with a molecular weight per double bond of 150 to

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3000, a functionality of 2 to 6, a hydroxyl number of 20 to 800, and an acid number of 0 to 15.

Aside from a pure polycondensation of  $\alpha,\beta$ -unsaturated carboxylic acid, preferably dicarboxylic acid with diols and/or triols,  $\alpha,\beta$ -unsaturated polyester diols (A) can be

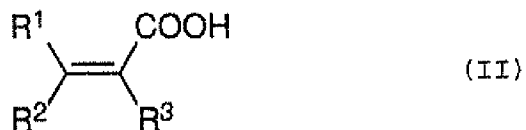
produced, for example, by converting polyvalent alcohol (B) with a compound (C), which contains an epoxy function and in addition a functional group that is reactive with respect to alcohols, into a compound (D) and converting this compound (D) with an  $\alpha,\beta$ -olefinic unsaturated carboxylic acid (E) into the compound (A) according to the invention or by directly converting an  $\alpha,\beta$ -olefinic unsaturated carboxylic acid (E) with (B) into a compound (A). As components (B) are preferably taken into consideration polyvalent, in particular bivalent, alcohols. Alcohols with 2 to 30, preferably 2 to 20 C atoms, like diols, such as 1,2-ethandiol, 1,2-propandiol, 1,3-propandiol, 1,4-butandiol, 1,5-pentandiol, 1,6-hexandiol, 1,2-hexandiol, 1,8-octandiol, 1,10-decandiol, 2-methyl-1,3-propandiol, 2,2-dimethyl-1,4-butandiol, 2,3-dimethyl-2,3-butandiol, 2-butene-1,4-diol, 1,2-cyclohexandiol, 1,4-cyclohexandiol, 1,3-cyclohexandiol, menthol, 1,4-cyclohexane dimethanol, hydroxy pivalic acid neopentyl glycol ester, diethylene glycol, methyl diethanolamine, like triols, such as glycerin, trimethylol propane, 1,2,4-butanetriol, and alcohols with at least four hydroxy groups, such as pentaerythritol, sorbitol, threitol, mannitol, dulcitol, or aromatic-aliphatic or aromatic-cycloaliphatic diols with 8 to 30 C atoms, wherein heterocyclic ring

systems or preferably isocyclic ring systems, like naphthalene or in particular benzol derivatives, such as hydrochinone, 4,4'-dihydroxy bisphenol, bisphenol A, twice symmetric ethoxylated bisphenol A., twice symmetrically propoxylated bisphenol A, high ethoxylated or propoxylated bisphenol A derivatives or bisphenol F derivatives, commercially available polyetherols, such as Lupranol®, Pluracol® (BASF Company), Systol® (BASF Company), Baycoll® (Bayer Company), Caradol® (Shell Company), Arcol® (Lyondell Company), Varanol® (DOW Chemical Company), Polypol® (Polioles Company), Tetracol® (Enichem Company), as well as mixtures of these compounds are taken into consideration as aromatic structures. Substance classes, for example, epoxidized olefins, glycidyl esters of saturated or unsaturated carboxylic acids, glycidyl esters of aliphatic or aromatic polyols, or epoxy alkyl halogenides can be used as substances (C) that react with hydroxyl groups (B).

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(+)-1-chloro-2,3-epoxy-2-methyl propane, (-)-1-chloro-2,3-epoxy-2-methyl propane, (1)-chloro-2,3-epoxy-2-methyl propane, in particular (+)-1-chloro-2,3-epoxy propane, (-)-1-chloro-2,3-epoxy propane, or (1)-chloro-2,3-epoxy propane, as well as mixtures of these compounds, for example, are suitable. The conversion into compound (D) according to

the invention can be carried out in a manner known per se, as described, for example, by C.A. May in "Epoxy Resins Chemistry and Technology," Marcel Dekker Inc., New York/Basel, 1988. These compounds are known per se. Polyglycidyl compounds of bisphenol-A type and glycidyl ethers of polyfunctional alcohols, for example, of butandiol, hexandiol, neopentyl glycol, 1,4-cyclohexane dimethanol, glycerin, and pentaerythrite, for example, Epikote 812, Epikote 828, and Epikote 162 of the Shell Company, or Heloxy 68 and Heloxy 107 of the Rhone-Poulenc Company, are particularly preferred. The compound (D) can be isolated from the reaction mixture according to known methods, for example, by extraction, precipitation, or spray drying, or can be advantageously used to produce compound (A). As compound (E) are taken into consideration above all carboxylic acids having the formula (II)



in which  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  represent hydrogen or  $\text{C}_1$ - $\text{C}_4$ -alkyl radicals, wherein maleic acid, fumaric acid, acrylic acid and methacrylic acid are preferred. Mixtures of different carboxylic acids such as these can also be used.



The conversion into compound (A) according to the invention can be carried out in a manner known per se, preferably at 90 to 130°C, particularly preferably at 100 to 110°C, and advantageously until the reaction mixture has an acid number of below 5 mg KOH/g.

The conversion of (B) with (E) into compound (A) according to the invention is particularly preferred.

As catalysts for the conversion of compound (D) with compound (E) can be used, for example, KOH, quaternary ammonium or phosphonium compounds, tertiary amines, phosphines, such as triphenyl phosphine, or Lewis bases, such as thiodiglycol.

The catalysts are preferably utilized in amounts of 0.01 to 5, particularly preferably 0.1 to 3% by weight with reference to compound (D).

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The additional use of a solvent and dilution agent is not required, but is preferred.

Suitable solvents or dilution agents are hydrocarbons, in particular toluol, xylol or cyclohexane, esters, in particular ethylene glycol acetate, ethyl acetate or butyl acetate, amides, in particular dimethyl formamide or N-methyl pyrrolidone, sulfoxide, in particular dimethyl sulfoxide, ketones, in particular methyl ethyl ketone or

cyclohexanone, ethers, in particular diisopropyl ether or methyl tert-butyl ether, or preferably cyclic ethers, in particular tetrahydrofuran or dioxane. The solvents or dilution agents can be used separately or as a mixture.

In order to prevent a premature polymerization, the conversion is carried out in particular with acrylic acid or methacrylic acid, suitably in the presence of small amounts of inhibitors. The usual compounds used to prevent thermal polymerization, for example, of the type of hydroquinone, hydroquinone alkyl ether, 2,6-di-tert-butyl phenol, N-nitrosamine or phenothiazine or phosphoric acid ester are taken into consideration. They are generally used in amounts of 0.005 to 0.5% by weight with reference to compound (E).

Compound (A) can be isolated from the reaction mixture according to known methods, for example, by extraction, precipitation, drying, or spray drying.

As already mentioned above,  $\alpha,\beta$ -unsaturated carbonyl compounds with additional functional groups, such as OH and  $\text{NH}_2$ , which are incorporated into the PUR network, lead to a particularly significant reduction of the MDA and TDA contents. As examples can be mentioned hydroxy ethyl acrylate or 3-(acryloyl-oxy)-2-hydroxy propyl methacrylate.

Polyols with integrated C=C double bonds in conjugation with the carbonyl group have a similar effect.

Those compounds (i), which dissolve well in isocyanates or are reactive with respect to isocyanates, are particularly preferred. (i) are preferably used in mixture with isocyanates.

In the method for producing polyurethane foamed materials according to the invention, the (i) are preferably used in an amount of 0.1 to 20% by weight, particularly preferably 0.5 to 10% by weight, with reference to the weight of polyurethane foamed materials.

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The polyurethane foamed materials obtained according to the invention have the particular advantage that the produced primary amines, in particular primary aromatic amines, are converted into a harmless form by means of the compounds (i) if required by means of hydrolysis. The polyurethane foamed materials, in particular mattresses, furniture upholstery, or carpet backing foam contain thus particularly preferred products from the conversion of primary and/or secondary amines, preferably aromatic amines, with the described compounds (i), that is, the  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes.

The use of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in polyurethane foamed materials with a reduced content of primary amines, in particular through reaction of compounds (i) with amino groups in the polyurethane foamed materials is accordingly preferred, and accordingly the use of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in polyurethane foamed materials for the conversion with primary amines.

The compounds described below are taken into consideration, for example, as isocyanates in the method for producing polyurethane foamed materials:

Aliphatic, cycloaliphatic, araliphatic and preferably aromatic organic isocyanates, preferably multifunctional, and particularly preferably diisocyanates, which are known per se, can be used as isocyanates.

The following should be named in detail: alkylene diisocyanates with 4 to 12 carbon atoms in the alkylene radical, such as 1,12-dodecandiisocyanate, 2-ethyl-tetramethylene diisocyanate-1,4, 2-methyl pentamethylene diisocyanate-1,5, tetramethylene diisocyanate-1,4 and preferably hexamethylene diisocyanate-1,6; cycloaliphatic

diisocyanates, such as cyclohexane-1,3- and -1,4-diisocyanate, as well as any desired mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate), 2,4- and 2,6-hexahydrotoluylene diisocyanate, as well as the corresponding isomer mixtures, 4,4'-, 2,2'- and 2,4'-dicyclohexyl methane diisocyanate, as well as the corresponding isomer mixtures, aromatic diisocyanates and polyisocyanates, such as, for example, 2,4- and 2,6-toluylene diisocyanate (TDI) and the corresponding isomer mixtures, 4,4'-, 2,4'- and 2,2'-diphenyl methane diisocyanate (MDI) and the corresponding isomer mixtures,

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naphthaline-1,5-diisocyanate (NDI), mixtures of 4,4'- and 2,4'-diphenyl methane diisocyanates, mixtures of NDI and 4,4'- and/or 2,4'-diphenyl methane diisocyanates, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl (TODI), mixtures of TODI and 4,4'- and/or 2,4'-diphenyl methane diisocyanates, polyphenyl polymethylene polyisocyanates, mixtures of 4,4'-, 2,4'- and 2,2'-diphenyl methane diisocyanates and polyphenyl polymethylene polyisocyanates (Roh-MDI) and mixtures of Roh-MDI and toluylene diisocyanates. The organic diisocyanates and polyisocyanates can be used separately or in form of mixtures thereof.

So-called modified polyvalent isocyanates, that is, products obtained by means of chemical conversion of organic diisocyanates and/or polyisocyanates are frequently used. As examples can be mentioned diisocyanates and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups. The following can be taken into consideration separately: organic, preferably aromatic polyisocyanates containing urethane groups with NCO contents of 33.6 to 15% by weight, preferably 31 to 21% by weight, with reference to the total weight, modified 4,4'-diphenyl methane diisocyanate, modified 4,4'- and 2,4'-diphenyl methane diisocyanate mixtures, modified NDI, modified TODI, modified Roh-MDI and/or 2,4- or 2,6-toluylene diisocyanate, wherein should be mentioned as dioxyalkylene or polyoxyalkylene glycols that can be used separately or as mixtures, for example: diethylene glycol, dipropylene glycol, polyoxyethylene, polyoxypropylene and polyoxypropylene polyoxyethylene glycols, triols and/or tetrols. Also suitable are prepolymers containing NCO groups with NCO contents of 25 to 3.5% by weight, preferably 21 to 14% by weight, with reference to the total weight, produced from, for example, polyester and/or preferably polyether polyols and 4,4'-diphenyl methane

diisocyanate, mixtures of 2,4'- and 4,4'-diphenyl methane diisocyanate, NDI, TODI, mixtures of NDI and isomers of MDI, 2,4- and/or 2,6-toluylene diisocyanates or Roh-MDI. Liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings with NCO contents of 33.5 to 15, preferably 31 to 21% by weight, with reference to the total weight, for example, based on 4,4'-, 2,4'- and/or 2,2'-diphenyl methane diisocyanate, NDI, TODI and/or 2,4- and 2,6-toluylene diisocyanate are also suitable.

The modified polyisocyanates can be utilized separately or mixed if required with unmodified organic polyisocyanates, such as, for example, 2,4'-, 4,4'-diphenyl methane diisocyanate, NDI, TODI, Roh-MDI, 2,4- and/or 2,6-toluylene diisocyanate.

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4,4'-, 2,4'- and/or 2,2'-diphenyl methane diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, NDI, hexamethylene diisocyanate and/or isophorone diisocyanate are preferably used as isocyanates in the mixtures according to the invention or according to methods, wherein these isocyanates can be used in any desired mixtures as well as also as in modified form already described.

As compounds that are reactive with respect to isocyanates, which usually have at least two reactive

hydrogen atoms, usually hydroxyl and/or amino groups, are suitably utilized those with a functionality of 2 to 8, preferably 2 to 6, and a molecular weight of usually 60 to 10,000. Polyether polyamines and/or preferably polyols selected from among the group of polyether polyols, polyester polyols, polythioether polyols, polyester amides, polyacetals containing hydroxyl groups, and aliphatic polycarbonates containing hydroxyl groups, or mixtures of at least two of the mentioned polyols have proven useful. Polyester polyols and/or polyether polyols, which can be produced according to known methods, are preferably utilized.

The polyester polyols have preferably a functionality of 2 to 4, in particular 2 to 3, and a molecular weight of usually 500 to 3000, preferably 1200 to 3000 and in particular 1800 to 2500.

The polyether polyols have a functionality of preferably 2 to 6 and usually molecular weights of 500 to 8000.

As polyether polyols are also suitable, for example, polymer-modified polyether polyols, preferably graft polyether polyols, in particular those based on styrene and/or acryl nitrile, which can be produced in situ by



polymerization from acryl nitrile, styrene or preferably mixtures of styrene and acryl nitrile.

The polyether polyols can likewise be utilized separately or in the form of mixtures like the polyester polyols. They can be mixed, in addition, with graft polyether polyols or polyester polyols as well as polyester amides, polyacetals and/or polycarbonates containing hydroxy groups.

High functional polyols, in particular polyether polyols based on high functional alcohols, sugar alcohols and/or saccharides as starter molecules are used therein as polyol components for polyurethane foamed materials, which can have isocyanate structures if required, and

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2-functional and/or 3-functional polyether and/or polyester polyols based on glycerin and/or trimethylol propane and/or glycols are used for flexible foams as starter molecules or as alcohols to be esterified. The production of polyether polyols is carried out therein according to known technology. Suitable alkylene oxides for the production of polyols are, for example, tetrahydrofuran, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, styrene oxide, and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides can be utilized separately, alternating one

after the other or as mixtures. Alkylene oxides are preferably used, which lead to primary hydroxyl groups in the polyol. As polyols are preferably utilized used those which are alkoxyated with ethylene oxide at the end of the alkoxylation, and which for this reason have primary hydroxyl groups. Polyols with a functionality of 2 to 2.2 and no wetting agents are preferably utilized to produce thermoplastic polyurethanes.

As compounds that are reactive with respect to isocyanates can be utilized chain extending and/or wetting agents. The addition of chain extending agents, wetting agents, or if required also mixtures thereof can be advantageous, for example, for the modification of the mechanical properties of the polyisocyanate polyaddition products produced with these substances, for example, the hardness. As chain extending and/or wetting agents can be used water, diols and/ triols with molecular weights of 60 to <500, preferably 60 to 300. As starter molecules are taken into consideration aliphatic, cycloaliphatic and/or araliphatic diols with 2 to 14, preferably 4 to 10 carbon atoms, such as, for example, ethylene glycol, propandiol-1,3 decandiol-1,10, o-, m-, p-dihydroxy cyclohexane, diethylene glycol, dipropylene glycol, and preferably butandiol-1,4, hexandiol-1,6 and bis-(2-hydroxy ethyl)

hydroquinone, triols, such as 1,2,4-, 1,3,5-trihydroxy cyclohexane, glycerin and trimethylol propane and low molecular polyalkylene oxides containing hydroxyl groups based on ethylene and/or 1,2-propylene oxide and diols and/or triols.

Insofar as chain extending agents, wetting agents, or mixtures thereof are utilized for the production of polyisocyanate polyaddition products, these are suitably utilized in amounts of 0 to 20% by weight, preferably 2 to 8% by weight, with reference to the total weight of the compounds that are reactive with respect to isocyanates, wherein thermoplastic polyurethanes are preferably produced without wetting agents.

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As compounds that are reactive with respect to isocyanates are only discussed those that do not fall under the definition of (i).

As catalysts are generally taken into consideration the usual compounds, for example, organic amines, for example, triethyl amine, triethylene diamine, tributyl amine, dimethyl benzylamine, N,N,N,N'-tetramethyl ethylene diamine, N,N,N,N'-tetramethyl butane diamine, N,N,N,N'-tetramethyl hexane-1,6-diamine, dimethyl cyclohexyl amine, pentamethyl dipropylene triamine, pentamethyl diethylene

triamine, 3-methyl-6-dimethyl amino-3-azapentol, dimethyl aminopropyl amine, 1,3-bisdimethyl aminobutane, bis-(2-dimethyl aminoethyl) ether, N-ethyl morpholine, N-methyl morpholine, N-cyclohexyl morpholine, 2-dimethyl aminoethoxy ethanol, dimethyl ethanolamine, tetramethyl hexamethylene diamine, dimethyl amino-N-methyl ethanolamine, N-methyl imidazole, N-(3-aminopropyl) imidazole, N-(3-aminopropyl)-2-methyl imidazole, 1-(2-hydroxyethyl) imidazole, N-formyl-N,N'-dimethyl butylene diamine, N-dimethyl aminoethyl morpholine, 3,3'-bis-dimethyl amino-di-n-propyl amine and/or 2,2'-dipiperazine diisopropyl ether, dimethyl piperazine, N,N'-bis-(3-aminopropyl) ethylene diamine and/or tris-(N,N-dimethyl aminopropyl)-s-hexahydrotriazine, or mixtures containing at least two of the mentioned amines, wherein also high molecular tertiary amines, such as those described, for example, in DE-A-28 12 256, are possible. The usual organic metal compounds, preferably organic tin compounds, such as tin(II) salts of organic carboxylic acids, for example, tin(II) acetate, tin(II) octoate, tin(II) ethyl hexoate and tin(II) laurate and dialkyl tin(IV) salts of organic carboxylic acids, for example, dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin maleate, and dioctyl tin diacetate can be utilized as catalysts for this purpose. Tertiary aliphatic and/or

cycloaliphatic amines can preferably be contained in the mixtures, particularly preferably triethylene diamine.

Generally known blow agents, such as, for example, substances having a boiling point within the range of  $-40^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  under normal pressure, gases and/or solid blow agents and/or water can preferably be used if required in the usual amounts as blow agents for the production of foamed polyurethanes, for example, carbon dioxide, alkanes and/or cycloalkanes, such as, for example, isobutane, propane, n-butane or isobutane, n-pentane and cyclopentane. Ethers, such as, for example, diethyl ether, methyl isobutyl ether and dimethyl ether, nitrogen, oxygen, helium, argon, laughing gas, halogenated hydrocarbons and/or partially halogenated hydrocarbons, such as, for example, trifluoromethane, monochlorotrifluoroethane, difluoroethane, /14 pentafluoroethane, tetrafluoroethane or mixtures containing at least two of the blow agents mentioned as example.

As auxiliary agents and/or additives should be mentioned, for example, surface active substances, foam stabilizers, cellular regulators, fillers, dyes, pigments, flame retardants, hydrolysis stabilizers, fungistatic and bacteriostatic acting substances.

The starting substances for the production of polyurethane foamed materials, for example, have already been described. The organic polyisocyanates and the compounds that are reactive with respect to isocyanates having a molecular weight of 60 to 10,000 g/mol are converted in such amounts that the equivalence ratio of NCO groups of polyisocyanates with respect to the sum of reactive hydrocarbons of the compounds that are reactive with respect to isocyanates amounts to between 0.5 and 5:1, preferably between 0.9 and 3:1, and in particular between 0.95 and 2:1.

It can likewise be advantageous if the polyurethanes contain at least partially bonded isocyanurate groups. In these cases, the ratio of NCO groups of polyisocyanates with respect to the sum of reactive hydrogen atoms is preferably selected between 1.5 and 60:1, preferably between 1.5 and 8:1.

The polyurethane foamed materials can be produced, for example, according to the one-shot process or the known prepolymer method, for example, with the aid of high pressure or low pressure technology in open or closed molding tools, reaction extruders, or belt conveyor systems.

It has shown to be advantageous to produce the polyurethane foamed materials according to the two-

component method and to join the compounds that are reactive with respect to isocyanates and if required the catalysts, blow agents and/or auxiliary agents and/or additives in the component A and to use the isocyanates and catalysts and/or blow agents as component B. The invention will be explained on the basis of the following examples.

Upholstery for furniture or automobiles, mattresses, in particular hospital mattresses, carpet backing foam of instrument panels or steering wheels or shoe soles are preferably produced according to the invention.

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#### Examples

Samples of soft foamed materials, which will be named below, were aged with humidity and heat in order to simulate conditions that can occur in the above-mentioned special applications. Sample cubes having an edge length of 3 cm of the foamed material to be tested were aged at 90°C and 90% relative air humidity for 72 hours in a climatic exposure test cabinet. Under these conditions occurred a hydrolytic cleavage of urethane and urea bonds and therewith the formation of primary aromatic amines. The formed amine was then extracted with the method developed by Prof. Skarping, L University. For this purpose, the foam was squeezed 10 times with 10 ml of

acetic acid (w = 1% by weight). The acetic acid was transferred into a 50 ml volumetric flask with the foam sample in compressed state. The procedure was repeated twice and the volumetric flask was filled with acetic acid up to the measuring mark. The MDA/TDA content of the joined extracts was then determined by means of capillary electrophoresis with UV detection. The MDA/TDA contents indicated in the table correspond to the absolute contents of the formed MDA/TDA in PUR foamed material.

#### Example 1

A polyurethane soft foamed material was produced by mixing 750 g of component A with 354 g of component B (index 90) and transferring the foaming mixture into an aluminum form (40 x 40 x 10 cm) tempered to 53°C, wherein the components arranged themselves as follows:

#### Component A

97 parts of a polyol with hydroxyl number (OH number) of 28 mg KOH/g, an average functionality of 2.3, and an ethylene oxide (EO)/propylene oxide (PO) ratio of 14/86,

3 parts of a polyol with an OH number of 42 mg KOH/g, an average functionality of 3, and a PO/EO ratio of 30/70,

3.31 parts of water,

0.8 parts of aminopropyl imidazole,

0.6 parts of Lupragen® N 107, OH number: 421 (BASF AG),



0.5 parts of Tegostab B 8631 (Goldschmidt).

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Component B

Mixture of polymer-MDI with a proportion of 50% and a difunctional MDI mixture with a proportion of 50%.

This system contains aminopropyl imidazole and Lupragen® N 107 (BASF AG) as incorporable catalysts. It was selected to clarify the special effectiveness of the added additives in PUR formulations with incorporable catalysts and catalytically active spacer polyols, such as the clear reduction of the MDA contents of foamed materials with addition of  $\alpha,\beta$ -unsaturated carbonyl compounds in comparison to the comparative systems shown in Table 1.

TABLE 1: COMPARISON OF MDA CONTENTS OF PUR SOFT FOAMED MATERIALS WITHOUT (FOAMED MATERIAL 1) AND WITH ADDITION OF  $\alpha,\beta$ -UNSATURATED CARBONYL COMPOUNDS (FOAMED MATERIALS 2 TO

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Foamed Material	1	2	3	4	5	6	7	8
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Hydroxy ethyl acrylate (% by weight with respect to (A))	-	10	-	-	-	-	-	-
3-(acryloyloxy)-2-hydroxypropyl methacrylate	-	-	10	-	-	-	-	-
Laromer® 8765 (% by weight with respect to (A))	-	-	-	10	-	-	-	-
Lupragen® VP 9198 (% by weight with respect to (A))	-	-	-	-	10	-	-	-
Trans-3-nonene-2-one (% by weight with respect to (B))	-	-	-	-	-	9.6	-	-
Cinnamic acid benzyl ester (% by weight with respect to (B))	-	-	-	-	-	-	7.2	-
Crotonic acid anhydride (% by weight with respect to (B))	-	-	-	-	-	-	-	2
Start time (s)	13	15	15	15	20	15	25	20
Gelling time (s)	80	90	95	95	95	85	95	95
Rising time (s)	100	110	150	115	110	120	120	140
4,4'-MDA (ppm) o.L.	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-MDA (ppm) o.L.	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-MDA (ppm) m.L.	397	31	59	55	43	223	155	98
2,4'-MDA (ppm) m.L.	687	86	134	118	105	391	321	184

(A): Addition of (i) to polyol component

(B): Addition of (i) to isocyanate component

o.L.: Extraction after processing of foamed material

m.L.: Extraction after humidity and heat aging for 3 days at 90°C and 90% relative air humidity in climatic exposure test cabinet

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Laromer® 8765 (BASF AG): bisacrylic acid ester containing OH groups with a molecular weight of 346.4 g/mol and an OH number of 323 mg KOH/g.

Lupragen® VP 9198 (BASF AG):  $\alpha,\beta$ -unsaturated polyester diol with an OH number of 336 mg KOH/g, an acid number of 0.7 and a molecular weight factor per double bond of 262, produced by means of polycondensation of maleic acid anhydride, 1,3-propandiol, and diethylene glycol in mol ratio of 1:1:1.

#### Example 2

A polyurethane soft foamed material, which was used as standard soft foamed material, was produced by mixing 750 g of component A with 349 g of component B (index 90) and transferring the foaming mixture into an aluminum mold (40 x 40 x 10 cm) tempered to 53°C, wherein the components arranged themselves as follows:

#### Component A

97 parts of a polyol with an OH number of 28 mg KOH/g, an average functionality of 2.3, and an EO/PO ratio of 14/86,

3 parts of a polyol with an OH number of 42 mg KOH/g, an average functionality of 3, and a PO/EO ratio of 30/70,

3.31 parts of water,

0.22 parts of 1,4-diazabicyclo(2,2,2)octane,

0.14 parts of Lupragen® N 206 (BASF AG),

0.5 parts of Tegostab B 8631 (Goldschmidt).

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#### Component B

Mixture of polymer-MDI with a proportion of 50% and a difunctional MDI mixture with a proportion of 50%.

TABLE 2: COMPARISON OF MDA CONTENTS OF PUR SOFT FOAMED MATERIALS WITHOUT (FOAMED MATERIAL 9) AND WITH ADDITION OF  $\alpha,\beta$ -UNSATURATED CARBONYL COMPOUNDS (FOAMED MATERIALS 10 AND 11)

Foamed Material	9	10	11
Hydroxy ethyl acrylate (% by weight with respect to (A))	-	10	
Laromer® 8765 (% by weight with respect to (A))	-	-	10
Start time (s)	13	16	-
Gelling time (s)	45	70	-
Rising time (s)	80	-	-
4,4'-MDA (ppm) o.L.	<1	<1	<1
2,4'-MDA (ppm) o.L.	<1	<1	<1
4,4'-MDA (ppm) m.L.	32	20	25
2,4'-MDA (ppm) m.L.	78	57	64

(A): Addition of (i) to polyol component  
(B): Addition of (i) to isocyanate component  
o.L.: Extraction after processing of foamed material  
m.L.: Extraction after humidity and heat aging for 3  
days at 90°C and 90% relative air humidity in  
climatic exposure test cabinet

### Example 3

A polyurethane soft foamed material, which was used as standard soft foamed material, was produced by mixing 750 g of component A with 275 g of component B (index 115) and transferring the foaming mixture into an open mold with a volume of 40 l, wherein the components arranged themselves as follows:

### Component A

100 parts of Lupranol® 2080 (BASF),  
2.65 parts of water,  
0.25 parts of Lupragen® N 101 (BASF),  
0.04 parts of Lupragen® N 206 (BASF),  
0.20 parts of tin dioctate,  
0.80 parts of silicone stabilizer BF 2370.

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Component B

Lupranat® T 80 (BASF)

TABLE 3: COMPARISON OF MDA CONTENTS OF PUR SOFT FOAMED MATERIALS WITHOUT (FOAMED MATERIAL 12) AND WITH ADDITION OF  $\alpha, \beta$ -UNSATURATED CARBONYL COMPOUNDS (FOAMED MATERIALS 13 TO 16)

Foamed Material	12	13	14	15	16
Hydroxy ethyl acrylate (% by weight with respect to (A))	-	5	-	-	-
3-(acrolloyloxy)-2-hydroxypropyl methacrylate (% by weight with respect to (A))	-	-	5	-	-
Laromer® 8765 (BASF AG) (% by weight with respect to (A))	-	-	-	10	-
Lupragen® VP 9198 (BASF AG) (% by weight with respect to (A))	-	-	-	-	10
2,4-TDA (ppm) o.L.	<1	<1	<1	<1	<1
2,6-TDA (ppm) o.L.	<1	<1	<1	<1	<1
2,4-TDA (ppm) m.L.	31	10	7	9	3
2,6-TDA (ppm) m.L.	8	6	4	5	2

(A): Addition of (i) to polyol component

(B): Addition of (i) to isocyanate component  
o.L.: Extraction after processing of foamed material  
m.L.: Extraction after humidity and heat aging for 3  
days at 90°C and 90% relative air humidity in  
climatic exposure test cabinet

The detection limit of the capillary electrophoretic  
determination amounted to 1 ppm.

The advantages according to the invention, that is,  
the clearly lower content of primary aromatic amines after  
storage under humid and hot conditions could thus be  
convincingly demonstrated.

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#### Patent Claims

1. A method for producing polyurethane foamed  
materials by converting isocyanates with compounds that are  
reactive with respect to isocyanates in the presence of  
blow agents and if required catalysts, additives and/or  
auxiliary agents, characterized in that the esterification  
is carried out in the presence of at least one of the  
following compounds (i):  $\alpha,\beta$ -unsaturated carboxylic acid,  
 $\alpha,\beta$ -unsaturated carboxylic acid derivative,  $\alpha,\beta$ -unsaturated  
ketone and/or  $\alpha,\beta$ -unsaturated aldehyde.

2. The method of claim 1, characterized in that  $R^1R^2-$   
 $C=CR^3COR^4$  having the following meanings

$R^1$ : H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,  
 $R^2$ : H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,  
 $R^3$ : H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl,  
 $R^4$ : H, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, (C<sub>6</sub>-C<sub>20</sub>)-aryl, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-OH, -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-OH,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl, -(C<sub>1</sub>-C<sub>12</sub>)-alkyl-NH<sub>2</sub>,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-NH<sub>2</sub>, -O-benzyl, O-aryl,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-COOH,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-CH(OH)-CH<sub>2</sub>-O-(CO)-CHCH<sub>2</sub>,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-O-(CO)-CHCH<sub>2</sub>,  
 -O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-CH(OH)-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl-  
 CH(OH)-CH<sub>2</sub>-O-(CO)-CHCH<sub>2</sub>

is used as (i).

3. The method of claim 1, characterized in that  
 acrylic acid, crotonic acid, isocrotonic acid, sorbic acid,  
 fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-  
 (acryloyloxy)-2-hydroxypropyl methacrylate, cinnamic acid  
 benzyl ester, trans-3-nonene-2-one, benzalacetone,  
 dibenzalacetophenone, 1-methyl benzalacetone,  
 crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or  
 $\alpha,\beta$ -unsaturated polyester diols produced by means of  
 polycondensation from maleic acid, fumaric acid,  
 methacrylic acid and/or acrylic acid with oligomeric diols,  
 such as butandiol, diethylene glycol, propylene glycol,



1,3-propandiol and/or triols, such as glycerin, with a molecular weight factor per double bond of 150 to 3000, a functionality of 2 to 6, a hydroxyl number of 20 to 800, and an acid number of 0 to 15 are particularly used as (i).

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4. The method of claim 1, characterized in that the (i) are preferably used in amounts of 0.01 to 20% by weight with reference to weight of polyurethane foamed material.

5. Polyurethane substances obtained according to a method of claim 1.

6. Polyurethane foamed materials containing products from the conversion of primary and/or secondary amines with  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes.

7. A utilization of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in polyurethane foamed materials with reduced content of primary amines.

8. A utilization of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in

polyurethane foamed materials for conversion with primary amines.